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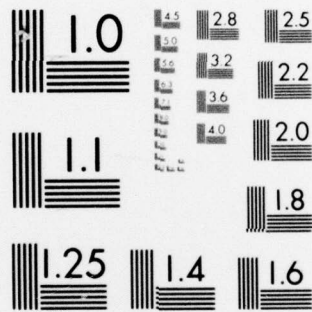


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THE STUDY OF CHEMILUMINESCENCE KINETICS

by

Harvey W. Yurow

Research Division

December 1977

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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SUMMARY

It has been experimentally determined that, with few exceptions, CW agents containing either halogen or cyano groups give chemiluminescence with luminol and hydrogen peroxide in basic solution. Structure-chemiluminescence correlations have been obtained for compounds with halogen bonded to carbon, sulfur, phosphorus, or arsenic.

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PREFACE

The work described in this report was authorized under Task 1L161102A71A02, Research in Support of Chemical Materiel. This work was started in July 1976 and completed in May 1977. The experimental data are recorded in notebook 9284.

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THE STUDY OF CHEMILUMINESCENCE KINETICS

I. INTRODUCTION.

The recent interest in chemiluminescence (CL) as a detection method at Chemical Systems Laboratory (CSL) began with work on a bio-alarm for the detection of bacteria. The resulting instrument employs a system containing luminol and hydrogen peroxide in basic solution, which produces CL with the hemin in bacteria.

During an investigation in the Analytical Branch of possible interferences with this system, it was found that a large number of organic compounds gave CL. Correlations between chemical structure and CL production were obtained.¹

Among the compounds giving CL were a number of CW agents, including chloroacetone and chloropicrin. As a result of this observation, the current study was initiated to discover which CW compounds either of historic or of current interest give CL or can be made to give CL by suitable modification. In addition, structure-CL correlations were investigated. These studies form the basis of this report.

II. EXPERIMENTAL.

A. Reagents.

The luminol (Aldrich) was 0.0025 M in 0.20 M sodium hydroxide. The hydrogen peroxide (Mallinckrodt, 30%) was diluted (1 + 99) with 0.002 M disodium ethylenediaminetetraacetate. The test compounds, most of which are commercially available or were obtained from Agents Research Section, CSL, were prepared as 1.0 mg ml⁻¹ (GB, 0.2 mg ml⁻¹) solutions in methanol or, if too unstable, in 2-propanol or acetone. (The latter solvent, giving an appreciable blank, was used only for phosgene.)

B. Equipment.

An Aminco-Bowman spectrophotofluorometer was used for all measurements.

C. Procedure.

Into a 1-ml microcell was pipetted 0.1 ml each of luminol and peroxide solutions. A 0.1-ml sample was introduced by hypodermic syringe, and the resulting CL curve was obtained at 420 nm. Results for the compounds, run in duplicate and corrected for molecular weight differences, are given in the table. The $t_{1/2}$ values are the times for the CL curves to grow to one-half and to decay to one-half ($t'_{1/2}$) of their maximum intensity values.

III. RESULTS AND DISCUSSION.

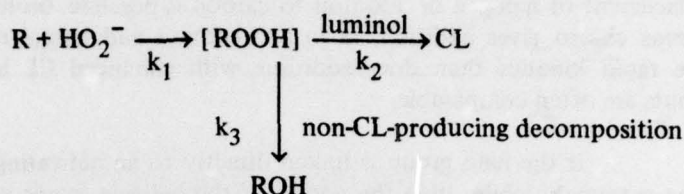
It is convenient to think of CL in the luminol-peroxide system as involving nucleophilic attack of hydroperoxide anion on an electrophilic organic compound, by either displacement or

Table. Chemiluminescence of CW Agents and Related Compounds

Compound	Relative intensity	t $\frac{1}{2}$ (S)	t' $\frac{1}{2}$ (S)
Benzyl bromide	120	0.2	0.4
Benzyl iodide	65	0.3	0.3
Ethyl bromoacetate	110	0.3	0.3
Methyl fluoroacetate	120	0.3	0.3
Ethyl-2-bromo-2-cyanoacetate	9700	15	130
Ethyl-2-chloroacetoacetate	6900	18	170
Ethyl chloroformate	280	0.2	0.4
3-Chloro-2-propanone	350	2	42
3-Bromo-2-butanone	1200	1	12
1,1-Dibromo-2-propanone	14000	0.5	6
1,3-Dibromo-2-propanone	56000	0.3	0.3
2-Chloroacetophenone	400	0.6	7
2-Bromoacetophenone	1300	1	7
Bromomethyl methyl ether	175	0.3	0.3
1,3-Dibromomethyl ether	620	0.3	0.3
Chloropicrin	12000	0.3	0.6
Bromopicrin	800000	0.3	0.6
Cyanogen chloride	240	0.3	0.4
Cyanogen bromide	1700	0.2	0.4
α -Bromophenylacetonitrile	4200	1	24
Phosgene	2800	0.2	0.3
Thiophosgene	33000	0.3	0.3
Phenyl isocyanide dichloride	21000	0.3	0.3
2,2'-Dichloroethyl sulfide	40	0.3	6
Trichloromethanesulfonyl chloride	400000	0.5	1.0
O-Nitrobenzenesulfonyl chloride	820	0.2	0.3
Methyl fluorosulfonate	860	0.3	0.4
Methyl chlorosulfonate	950	0.2	0.5
Dimethyl sulfate	80	0.2	0.4
Chlorovinyl dichloroarsine	4800	0.2	0.2
Phenarsazine chloride	7500	0.3	0.5
Diphenyl cyanoarsine	450	0.2	0.3
Phenarsazine cyanide	7200	0.2	0.4
Isopropyl methylphosphonofluoridate	550	0.3	0.3
Diethyl chlorophosphate	15000	0.3	0.3
Ethyl dichlorophosphate	44000	0.4	0.4
Diethyl chlorothiophosphate	1300	0.3	0.3
Ethyl dichlorothiophosphate	18000	0.3	0.3
O-Chlorobenzylidene malononitrile*	17000	0.3	2.5

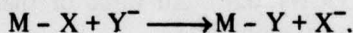
* After treatment with 0.1 volume of 1% aqueous sodium borohydride for 2 minutes.

addition, to give an intermediate hydroperoxide. This intermediate, whose oxidizing power depends upon electron withdrawing groups in the molecule, then oxidizes the luminol to produce CL,



The shape of the CL curve and hence the CL intensity will depend upon the relative values of k_1 , k_2 , and k_3 . These in turn will depend upon the structure of R. A complicating factor is that R may also be subject to nucleophilic attack by water and hydroxide anions present in the solution. This will be considered in more detail below.

In nucleophilic displacement reactions, e.g.,



There are three factors that essentially control the reaction. First is the electronegativity difference between M and X as given by Paulings' electronegativity values.² The greater the partial positive charge on M, the more readily it will be subject to nucleophilic attack. Also important is the leaving ability of Y. Generally, the stronger the acid H-Y, the better is the leaving ability of Y. A third factor is the size of M. As atom M becomes larger, it has greater polarizability and therefore less repulsion to nucleophilic attack by Y^- .

Most chemical warfare agents are either the labile halogen or the cyano type. The labile halogen class can conveniently be divided into groups, depending upon whether the halogen is linked directly to carbon, sulfur, phosphorus, or arsenic.

A. Halogen-Carbon Bond.

Because of a relatively small electronegativity difference between carbon and halogen, specifically 0.5 and 0.3 for chlorine and bromine, respectively, this bond is usually relatively stable to nucleophilic attack by hydrogen peroxide anion, unless activated by an electron-withdrawing group in proximity. As a result, the fractional positive charge on the carbon is increased and it is more readily attacked by a nucleophile. If the halogen is linked by a methylene group to the activating group, as in RCH_2X , then the leaving group ability of the halogen atom influences CL strongly. Relative leaving group abilities for $\text{S}_\text{N}2$ reactions are usually in the order $\text{F} \ll \text{Cl} \ll \text{Br}, \text{I}$.

The lachrymators benzyl chloride, bromide, and iodide give very weak CL, as expected from the relatively weak electron-withdrawing effect of the benzyl moiety. The low CL intensity for the agent ethyl bromoacetate is probably the result of two factors: (1) a side reaction involving the cleavage of the ester to CL inactive bromoacetate anion and (2) the relatively weak inductive effect of the intact ester group on intermediate hydroperoxide formed by displacement of the bromo group. By contrast, strong CL is given by ethyl-2-bromo-2-cyanoacetate because of the strong activating effect of the cyano moiety. Results for chloro and bromo compounds are as expected, with bromo being a much better leaving group.³ Bromopicrin gives much stronger CL

than chloropicrin because bromo is displaced from the former and nitro is displaced from the latter.⁴ However, total CL outputs for both compounds are comparable. It appears that when displacement of halogen or addition to carbon is possible, bromo preferentially gives displacement, whereas chloro gives addition, as in haloketones and halonitriles. Displacement frequently gives more rapid kinetics than does addition, with enhanced CL intensity; but, here again, total CL outputs are often comparable.

If the halo group is linked directly to an activating group, such as cyano or keto and hence extremely labile, then the nature of the halogen is not important. Thus, cyanogen chloride, bromide, and iodide give similar CL curves. Other CW agents in this group include phosgene and thiophosgene and ethyl chloroformate. All are categorized by rapid kinetics. Differences in CL intensities are probably the result of competing nucleophilic reactions with water and hydroxide.

Structure and CL of the compounds may be compared using the Taft treatment.⁵ Polar substituent constants are available for the aliphatic series RX and involve the inductive effect of activating group R on halogen X. The CL series benzyl bromide < bromoethyl methyl ether < bromoacetone agrees with the order of substituent constants: $C_6H_5CH_2$, 0.22; CH_3OCH_2 , 0.52; and CH_3COCH_2 , 0.60. All three of these moieties have small steric substituent constants, so that polar effects predominate.

The compounds ethyl chloroformate and acetyl chloride give lower CL than expected based upon high polar substituent values; i.e., CH_3OOC , 2.00, and CH_3CO , 1.65. Here, the extreme lability of the halogen results in significant non-CL-producing side reactions with water and hydroxide. Therefore, a plot of CL intensity versus polar substituent constants for halogen compounds (corrected for steric differences) will give a bell-shaped curve. Compounds such as chloroacetonitrile ($CNCH_2$, 1.30) cannot be included in this treatment because a different mechanism, addition rather than displacement, may be operative.

One halide that does not give CL is bis(2,2'-dichloroethyl)sulfide, which is probably the result of the halogen not being in proximity to the sulfur atom.

B. Halogen-Sulfur Bond.

Although, on the basis of electronegativity difference, carbon-halogen and sulfur-halogen bonds give identical values (0.5), sulfur, being a larger atom than carbon, has greater polarizability and hence less repulsion to nucleophilic attack by a negatively-charged species. The two classes of CW agents in this group are the sulfonyl chlorides including trichloromethanesulfonyl chloride (perchloromethyl mercaptan), and the methyl halosulfonates. The former compound is remarkable in giving, along with bromopicrin and aryldiazonium salts, the most intense CL of any organic compounds tested. The methyl halosulfonates give moderate CL with rapid kinetics, and the nature of the halogen group does not affect CL appreciably.

C. Halogen-Phosphorus Bond.

The large electronegativity difference (0.9 for chlorine) results in high lability for this bond. However, the fluoro compounds are sufficiently less labile than the other halogens so as to be powerful CW agents. This is due to greater strength of the P-F bond and poorer leaving ability of the fluoro group.

The relatively low CL of isopropyl methylphosphonofluoridate (GB) may be related to the steric effect of the bulky isopropyl group, as diisopropyl chlorothiophosphate gives only about one-fifth of the CL intensity of di-n-propyl chlorothiophosphate.

D. Halogen-Arsenic Bond.

On the basis of the large electronegativity difference, the halogen in haloarsenicals should be quite labile and subject to solvolytic side reactions with consequent lowering of CL intensity. Therefore, the moderate CL of dichlorovinyl chloroarsine and phenarsazine chloride (DM) are as expected. Another factor that would contribute to the decreased CL yield for these compounds is the relatively low electron-withdrawing ability of the organoarsenic moiety, so that intermediate hydroperoxides would be weaker oxidants. However, the rapid CL kinetics for these compounds lead one to suspect that a preferential free radical reaction may be occurring.

The cyano class includes diphenyl cyanoarsine, phenarsazine cyanide, hydrogen cyanide, and o-chlorobenzylidene malononitrile (CS). The two arsenic compounds give CL curves similar to that for phenarsazine chloride but of lower CL intensity. Although both displacement of and addition to the cyano group by a hydroperoxide anion are possible, it is suspected that the former predominates as the CL kinetics are similar to those for DM.

That CS gives weak CL compared to malononitrile is undoubtedly due to the double bond, where preferential epoxidation by a hydroperoxide anion may take place.⁶ The double bond is readily reduced by sodium borohydride or cyanoborohydride with consequent enhancement of the CL intensity, approaching that of malononitrile itself.

Hydrocyanic acid does not give CL, undoubtedly because it is ionized in basic solution to an anion which reacts only slowly, if at all, with hydroperoxide anion because of charge repulsion.

In summary, one may note that most CW agents are strong electrophiles, which probably have their physiological effect by reactions with nucleophilic centers in the body. As CL with the luminol peroxide system is also based upon a nucleophilic reaction, it is understandable why so many CW agents give CL and why CL may be employed as a general detection method for this class of compounds.

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